PREPARATION AND CHARACTERIZATION OF POLYIMIDE/INORGANIC COMPOSITE FILMS AS SOLID DIELECTRICS

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PREPARATION AND CHARACTERIZATION OF POLYIMIDE/INORGANIC COMPOSITE FILMS AS SOLID DIELECTRICS

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DECLARATION

I hereby declare that I have conducted, completed the research work and written the dissertation entitled "Preparation and Characterization of Polyimide/Inorganic composite films as solid dielectric". I also declare that it has not been previously submitted for the award for any degree or diploma or other similar title for any other examining body or University.

Name of student: ASLIZA BINTI ALIAS **Signature:**

Date:

Witnessed by

Supervisor: PROF. MADYA AHMAD BADRI BIN ISMAIL **Signature:**

Date:

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LIST OF ABBREVIATIONS

PI	polyimide
MIM	metal-insulator-metal
RC	resistance-capacitance
IC	integrated-circuit
Al_2O_3	aluminium oxide/alumina
$BaTiO_3$	barium titanate
TiO_2	titanium oxide/titania
ZrO_2	zirconium oxide/zirconia
PAA	poly(amic acids)
ODA	4, 4-oxydianiline
PMDA	pyromellitic dianhydride
DMAc	dimethylacetamide
APS	3-aminopropyltrimethoxysilane
XRD	X-ray diffraction
FTIR	Fourier Transform Infrared Spectroscopy
SEM	Scanning Electron Microscopy
TGA	Thermogavimetry analysis

LCR	Inductance (L), Capacitance (C), Resistance (R)
BDAPD	α,α′-bis[3,5-dimethyl-4-(4-aminophenoxy)phenyl]-1,4-diisopropylbenzene
RT	room temperature
MHD	magnetohydrodynamics
PTC	positive temperature temperature
MLCC	multilayer ceramic capacitors
APTS	3-aminopropyltriethoxysilane
IR	Infrared

LIST OF SYMBOLS

k	dielectric constant
%	percent
Hz	Hertz
MHz	mega-hertz
kHz	kilo-hertz
ε	permittivity
ε_o	permittivity of vacuum
C’	capacitance of a material
C	capacitance of a vacuum
t	thickness
A	contact area
Q, q	charge
d	distance
p	dipole moment
α	polarizability
α_e	electronic polarizability
α_i	ionic polarizability
α_d	dipolar polarizability

α_s	space charge polarizabilty
E	electric field
N	number of particles in unit volume
tan δ	conduction loss
f	Farads
V	Voltage
^oC	degree Celsius
W/(m.K)	watts per meter Kelvin
µm	micro meter
nm	nano meter
h	hour
min	minute
^{o}	degree
wt%	weight percent
k	kilo
f	frequency
T_5, T_{10}, T_{20}, T_{30}	degradation/decomposition temperature at 5%, 10%, 20% and 30% weight loss, respectively

g/mol	grams per mole
mmHg	millimetres of mercury
g/mL	grams per milliliter
^{o}F	*Fahrenheit*

PENYEDIAAN DAN PENCIRIAN FILEM KOMPOSIT POLIIMIDA/TAK-ORGANIK SEBAGAI DIELEKRIK PEPEJAL

ABSTRAK

Permintaan yang memuaskan ke atas dielektrik filem-nipis pepejal dengan pemalar dielektrik tinggi untuk penggunaan dalam fabrikasi kapasitor telah dikaji. Dalam kajian ini, komposit filem poliimida/tak-organik telah dihasilkan dengan menggabungkan bahan tak-organik yang berlainan jenis; Al_2O_3, $BaTiO_3$, TiO_2 dan ZrO_2 ke dalam poliimida (PI) yang berasas daripada monomer PMDA dan ODA melalui kaedah pengultrabunyian. Struktur kimia, morfologi, dielektrik dan sifat termal telah dikaji oleh FTIR, XRD, SEM, meter LCR dan analisis termal (TGA). Spektra FTIR menunjukkan pengimidaan lengkap dan semua puncak pencirian kumpulan imida diperhatikan dalam spektra filem komposit PI/tak-organik. Difraktogram XRD menunjukkan komposit PI/tak-organik mempamerkan puncak yang setara dengan bahan tak-organik induk, menunjukkan bahawa struktur kristal bahan tak-organik kekal tidak berubah dan stabil setelah didopkan ke dalam matrik poliimida. Mikrograf-mikrograf SEM menunjukkan taburan seragam bagi bahan tak-organik Al_2O_3, $BaTiO_3$ dan TiO_2 dalam matrik poliimida melalui kaedah pengultrabunyian dan ejen gandingan 3-aminopropyltrimethoxysilane kecuali bagi komposit PI/ZrO_2. Sementara itu, pemalar dielektrik dan kehilangan dielektrik filem komposit PI/tak-organik umumnya meningkat dengan penambahan kandungan bahan tak-organik. Kandungan bahan tak-organik tidak mempunyai kesan yang ketara ke atas suhu degradasi komposit PI/tak-organik. Berdasarkan kajian, komposit PI/$BaTiO_3$ adalah PI/tak-organik yang paling berpotensi sebagai dielektrik pepejal kerana ia mempunyai pemalar dielektrik yang paling tinggi iaitu 21.1 dengan

kandungan 30wt% pada 1MHz dan kehilangan dielektrik yang paling rendah diikuti oleh PI/TiO_2 dan PI/Al_2O_3. Walaupun PI/ZrO_2 mempunyai kestabilan termal yang paling tinggi, perbezaan pengembangan termal yang sangat tinggi antara PI dan ZrO_2 menyebabkan rekahan makro dan membuatkan ia tidak sesuai sebagai dielektrik pepejal.

PREPARATION AND CHARACTERIZATION OF POLYIMIDE/INORGANIC COMPOSITE FILMS AS SOLID DIELECTRICS

ABSTRACT

Considerable demand for solid thin-film dielectrics with high dielectric constants for use in the fabrication of capacitors has been observed. In this study, polyimide/inorganic composite films were prepared by incorporating different type of inorganic materials; Al_2O_3, $BaTiO_3$, TiO_2 and ZrO_2, into polyimide (PI) derived from PMDA and ODA monomers via ultrasonication method. Chemical structure, morphology, dielectric and thermal properties were investigated by Fourier transform infrared (FTIR) spectroscopy, X-ray diffraction (XRD), scanning electron microscopy (SEM), LCR meter and thermal gravimetric analysis (TGA). FTIR spectra showed complete imidization, and all characteristic peaks of the imide groups are observed in PI/inorganic composite films. XRD diffractogram reveals that the PI/inorganic composite exhibits peaks similar to those of parent inorganic materials, indicating that the crystal structure of inorganic materials remain unchanged and stable after being doped into the PI matrix. SEM micrographs displays a uniform distribution of inorganic particles of Al_2O_3, $BaTiO_3$ and TiO_2 in the PI matrix by means of ultrasonication method and 3-aminopropyltrimethoxysilane coupling agent except for PI/ZrO_2 composite. Meanwhile, the dielectric constants and dielectric losses of PI/inorganic composite films generally increase with the addition of inorganic content. The content of inorganic materials does not have significant effect on the degradation temperature of the PI/inorganic composites. Based on the study, PI/$BaTiO_3$ composite is the most potential PI/inorganic composite as solid dielectric as it possesses highest dielectric constant which is 21.1 with 30wt% content at 1MHz

and lowest dielectric loss followed by PI/TiO_2 and PI/Al_2O_3. Even though PI/ZrO_2 exhibits highest thermal stability, a very high thermal expansion mismatch between PI and ZrO_2 induces macro cracks and makes it not suitable as a solid dielectric.

CHAPTER 1

INTRODUCTION

1.1 Research Background

Electronic industry is one of the industrial sectors which contribute to the technology advancements when at the same time become most affected as the technology is rapidly growing. Recent years have seen electronic products that are thinner, lighter, and more compact, at the same time exhibiting rapidly improving performance. Electronic products are getting lighter and smaller to make them portable and meet the demand of the consumers. Electronic devices, circuits, appliances are designed to be smaller, multifunctional and capable to functions well in extreme condition such as at higher temperature and under stress. Most of electronic products comprise of electric circuits and electronic devices that connect to one another.

Smaller electronic components have been produced to develop more compact electronic circuits and devices. Dielectric material is one of the major components in most of electronic device. Therefore, to keep up with these advancements, most of dielectric materials are fabricated in thin film shape. In satisfying these requirements, plastic is one of the preferred materials used as dielectrics in electronic devices. Plastic offers strong resistivity, ease of processability, high flexibility, low hygroscopic property, and higher insulation resistance than paper (Deligoz et al., 2006). Polyimide (PI) is one of the commercially used plastic dielectrics in electrical industries. They have attracted considerable attention because of their ability to withstand high temperatures, as well as their excellent chemical resistance, high

thermal stability, good mechanical strength, favourable dielectric properties, leakage current density, and high dielectric breakdown strength (Deligoz et al., 2006; Wang et al., 2009). Polyimide is widely used in application requires low dielectric constant (k) as it possess low dielectric constant (around 3 when measured at 1 MHz) (Xie et al., 2005; Wang et al., 2009) and hence limits its performance in applications which demand much higher dielectric constants.

On the other hand, in higher k application, inorganic-based dielectrics are widely utilized. They exhibit excellent thermal stability, functional properties such as dielectric and magnetic properties (Wang et al., 2009). Although inorganic materials offer higher dielectric constant values compared with plastic, the sizes and shapes in which they are available are limited because of their high brittleness and fragility. Such features make shaping inorganic materials into films and smaller sizes difficult.

Both dielectrics with low and high dielectric constant are essential in electronic industries. A high-k dielectric material has a high permittivity due to its potential at holding charge; they are the preferred dielectric for capacitors such as embedded capacitors and metal-insulator-metal (MIM). High-k dielectrics are also used in memory cells that store digital data in the form of charge. A low dielectric constant, on the other hand, is a dielectric that has a low permittivity or low ability to polarize and store charge (Jiang et al., 2006; Lu et al., 2007). Low-k dielectrics are very good insulators for isolating signal-carrying conductors from each other, fast signal propagation, interlayer dielectric to reduce the resistance-capacitance (RC) time delays, crosstalk and power dissipation in the high density and high speed integrated (Maier, 2001). Thus, low-k dielectrics are a necessity in very dense multi-

layered IC's, wherein coupling between very close metal lines need to be suppressed to prevent degradation in device performance.

As the technology is advancing rapidly, the capability of electronic devices to perform at their best especially in much extreme condition such as at higher temperature, under high stress and long lasting have been challenged. Nowadays, it is often seen the dielectric materials in thin film. Most of thin film dielectrics are made of polymers which majority of them possesses low dielectric constant and poor thermal stability. The problem arises when there are demands on thin film dielectric with higher value of dielectric constant and good thermal stability for higher performance application. Therefore, to meet the growing demand on smaller and better performance of the dielectrics, organic-inorganic composites has been introduced and studied.

Several studies on composites consisting of inorganic particles embedded into a polymer matrix have been conducted. Introducing high dielectric constant ceramic particles into a polymer matrix produces composites with dielectric constants higher than that of original polymer, but with similar processability and flexibility (Bai et al., 2000; Kuo et al., 2001; Xie et al., 2005). By integrating the advantages of the two phases, the composite materials can offer performance far beyond those of the individual constituents.

In this study, PI/inorganic composite films were prepared to produce composite films with various values of dielectric constants while improving the thermal stability. Different types of inorganic particles; alumina (Al_2O_3), barium

titanate ($BaTiO_3$), titania (TiO_2) and zirconia (ZrO_2) were selected and incorporated into PI matrix. The selection of inorganic materials is based on their great dielectric constant, low dielectric loss and high thermal stability. Alumina has a superior insulating qualities, good thermal conductivity, low electrical loss, low cost and considerably quite high dielectric constant which is around 8-10 (Wu et al., 2005; Malec et al., 2010). Meanwhile, zirconia is widely known for its high resistance towards thermal, chemical and mechanical while at the same time possessing dielectric constant in a range of 12-28 (Harrop and Wanklyn, 1967; Izumi et al., 1989). As for both $BaTiO_3$ and TiO_2, besides exhibiting great thermal stability, they also possessing high dielectric constant value especially $BaTiO_3$ which is around 2000-5000 while TiO_2, 14-114 (Viswanathan, 2006). In addition, $BaTiO_3$ also has low dielectric loss which is one of the desirable dielectric properties.

In the preparation on PI/inorganic composites films of this study, different loading (10wt%, 20wt% and 30wt%) of Al_2O_3, $BaTiO_3$, TiO_2 and ZrO_2 particles were incorporated into the PI matrix, respectively. The preparations, chemical structure, morphology, thermal and dielectric properties of the composite films were discussed. The effects of inorganic type and loading on the properties of the composites were investigated. The effect of inorganic particle agglomerations in composite on dielectric properties was also studied.

1.2 Problem Statement

There are several previous studies on PI/Al_2O_3 that have been reported, however the study on dielectric constant and dielectric loss of the composite is seldom reported. Li et al. (2007) reported that the dielectric constant of PI/Al_2O_3

composite with 20wt% content reported is around 3.1 which very low whereby such value usually falls in dielectric constant range of polyimide which is around 3-3.5 (Xie et al., 2005; Wang et al., 2008; Wang et al., 2009). On the other hand, some studies on preparation of PI/TiO_2 composites using different monomers and various methods have been reported. Most of the studies are focusing on refractive index, thermal and mechanical properties of the composites (Tsai et al., 2006; Tsai et al., 2008; Yu et al., 2011). Nevertheless, a few studies on dielectric constant of PI/TiO_2 composites have been reported (Koytepe et al., 2008; Yu et al., 2011). However, both works used different monomers and different methods in producing PI/TiO_2. The dielectric constant of PI/TiO_2 composite with 30wt% reported by Yu et al. (2011) is extremely low which only around 2.25 when measured at 1MHz. Wang et al. (2009) reported the dielectric constant of PI/$BaTiO_3$ composite at 1MHz with 30wt% is around 10 which relatively low. In another study on PI/$BaTiO_3$ composite, the dielectric constant values are only measured at low frequency range; 100Hz to 10kHz.

Therefore this study is to prepare these PI/inorganic composites by using the same polyimide based on PMDA and ODA monomers and coupling agent of 3-aminopropyltrimethoxysilane. The thermal curing process is also taken into account in preparing the composite films with minimum warping and shrinkage. The dielectric properties of the PI/inorganic composites are expected to be improved as compared to previous studies.

1.3 Objectives

Overall, this study covers on the preparation and characterization of polyimide/inorganic composite films in which inorganic materials used consists of alumina, barium titanate, titania and zirconia. The composites are expected to exhibit a range of dielectric constant values from low to high.

The objectives of this study are simplified as stated below:

i) To synthesize polyimide via two-steps poly(amic acids) (PAA) process based on 4, 4- oxydianiline (ODA) and pyromellitic dianyhydride (PMDA) in dimethylacetamide (DMAc) solvent.

ii) To study the effects of different mixing methods and 3-aminopropyltrimethoxysilane (APS) coupling agent on the dispersion level of Al_2O_3, dielectric and thermal properties of the PI/Al_2O_3 composites before selecting the best mixing method to proceed with PI/$BaTiO_3$, PI/TiO_2 and PI/ZrO_2 composite preparation.

iii) To study the chemical structure of the composites and the effect of inorganic loading incorporated into PI matrix on dielectric and thermal properties. The effect of different type of inorganic materials used also studied and compared.

1.4 Scope of Work

Fig. 1.1 shows the summary of work covered in this study. First stage of this study covers the synthesis of poly(amic acids) solution, the treatment of inorganic materials and preparation of PI/Inorganic composite films. The next stage involves the characterization of inorganic materials, poly(amic acids), polyimide and PI/inorganic composite films studied through FTIR and XRD. The morphology of polyimide and PI/inorganic composite films is also studied. In the last stage of this study, dielectric and TGA testing of PI and PI/inorganic composites are performed on LCR meter and Perkin Elmer Pyris 6. The results are analyzed and discussed.

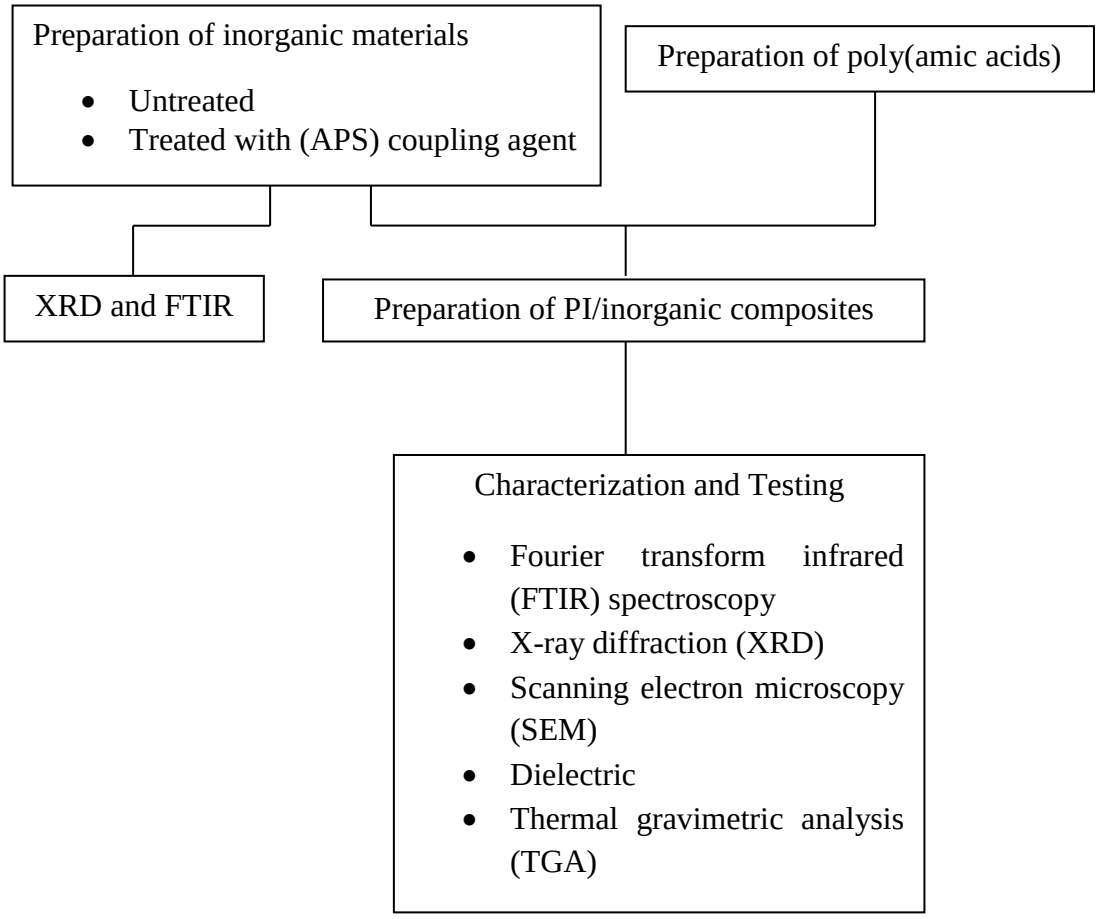

Fig. 1.1. Summary of work covered in this study.

CHAPTER 2

LITERATURE REVIEW

2.1 Dielectric materials

Dielectric materials are electrical insulators which are used principally in capacitors and electrical insulators (Pollock, 1993). They become polarized under the influence of an external electric field (Ku and Liepins, 1987; Sirdeshmukh et al., 2006). Ceramic and polymers are dielectric materials by the fact that they contain virtually no free charges and therefore are electrical insulators (Naumann, 2008).

Dielectric materials can be in solid, liquid, gas and vacuum form. However, solid dielectric is the most commercialized due to its stability and easy to handle. Mica, paper, polyethylene, poly (vinylidene fluoride), polyimide, polyester film, metalized paper and propylene are the common type of solid dielectrics (Ku and Liepins, 1987; Xie et al., 2004; Lin and Wang, 2007; Popielarz and Chiang, 2007). Most of them are ceramic and polymer base or the combination of both which better known as organic-inorganic composites. Oil and liquid gas are the example for liquid dielectric which is widely applied in high voltage application (Meyrueix et al., 1982).

The properties of an ideal dielectric material are to resist the flow of current and good at holding charges. Despite this, tunnelling current, cross talk can occur at sufficiently high voltages (Hawker et al., 2000; Morgen et al., 2000; Martin et al., 2000). This is due in practice; all dielectrics do have some conductivity, which generally increases with increase in temperature and applied field (Naumann, 2008). The leakage charge will occur at critical field. In most cases, high-k dielectrics are most likely to experience this phenomenon, than do the materials with low-k (Das-

Gupta and Doughty, 1988; Subodh et al., 2007). High-k able to store more charges and becomes conductive when some critical magnitude of applied field and cause current leakage and hence lead to dielectric breakdown (Naumann, 2008). The geometry of the dielectric, shape and materials of the electrode, the nature of the medium surrounding the dielectric, the time variation of electric field and other factors also affected the critical applied field (Smyth, 1955; Ku and Liepins, 1987; Pollock, 1993).

2.2 Dielectric constant

Dielectric constant is a measure of the effectiveness of the materials on a capacitor. It is the ratio of the capacitance of a capacitor filled with dielectric material to that of an identical but empty capacitor. Dielectric constant also indicates the ability of the dielectric to polarize. On the other hand, it also relates to the permittivity of the materials. Permittivity is a quantity that describes the effect of a material on an electric field; the higher the permittivity, the more the material tends to reduce any field set up in it (Ku and Liepins, 1987). In other words, permittivity is a measure of the ability of a material to be polarized upon the presence of electric field (Pollock, 1993). Equivalently, dielectric material also reduces the field by becoming polarised. Therefore, it is convenient to define a relative dielectric constant (k) of a material as the ratio of its permittivity to the permittivity of vacuum and is represented by the equation:

$$k = \frac{\varepsilon_o}{\varepsilon} \qquad (2.1)$$

Where k is the dielectric constant of the material while ε is the permittivity of the dielectric material and ε_o is the permittivity of vacuum (Smyth, 1955). The diagram in Fig. 2.1 illustrates the definition of the dielectric constant. Consequently, it can be

concluded that the greater the polarization generated by the materials in electric field, the higher the dielectric constant will be.

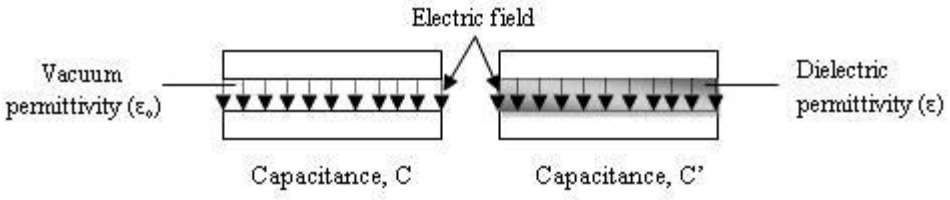

Fig. 2.1. The illustration of dielectric constant definition.

The dielectric constant also defines capacitance of any capacitor comprising a layer of dielectric sandwiched between two electrodes. It can be represented by the equation:

$$k = \frac{C'}{C} \tag{2.2}$$

$$C' = kC \tag{2.3}$$

$$C = \frac{A\varepsilon_o}{t} \tag{2.4}$$

$$C' = \frac{k\varepsilon_o A}{t} \tag{2.5}$$

where C' is the capacitance of the dielectric material and C is the capacitance of a vacuum while A is the contact area between the electrode and dielectric while t is the thickness of the dielectric material (Smyth, 1955; Naumann, 2008).

2.3 Dielectric polarization

The electrical properties of dielectric materials are determined by their ability to polarize and form electric dipoles under the action of external field. The electrical dipole can be assumed as having two opposite charges which are positive and negative charge q separated by certain distance d and the dipole moment is defined as p=qd (Wert and Thomson, 1970; Naumann, 2008). The electric dipole acquired by an atom or a molecule proportional to the applied field. The proportionality constant which is called as polarizability, α, is defined by p=αE, where p= dipole moment induced by the local electric field, E (Viswanathan, 2006; Sirdeshmukh et al., 2006). As the electric dipole acquired by the number of particles (atoms, ions or molecules), the polarization is well defined as the electric moment/dipoles per unit volume of the dielectric which is represented by

$$p=N\alpha E \qquad (2.6)$$

where N is the number of particles in unit volume (Pollock, 1993; Sirdeshmukh et al., 2006). In a most general case, polarizability,α , has four possibility components which expressed by the summation:

$$\alpha = \alpha_e + \alpha_i + \alpha_d + \alpha_s \qquad (2.7)$$

where,

α_e = electronic polarizability

α_i = ionic polarizability

α_d = dipolar polarizability

α_s = space charge polarizability

The electronic polarizability, α_e, is one of the main polarization mechanisms within dielectric material which arises from the displacement of the electron's orbit relative to the positive charged nucleus caused by the distortion of electronic orbits (Ku and Liepins, 1987; Viswanathan, 2006). The presence of an electric field, E distorts the electron's orbit and displaces its center from the positively charged nucleus creating a dipole moment (Smyth, 1955; Wert and Thomson, 1970; Karasz, 1972; Ku and Liepins, 1987). Electronic polarizability occurs at a high frequency range whereby the space, ionic and dipolar polarization are absent (Fig. 2.2).

Ionic and dipolar polarizability occur in materials possessing ions and permanent dipoles respectively. Ionically bonded compounds have oppositely charged ion cores; anions and cations which cancel each other when no electric presence. Upon the presence of electric field, these cations are displaced from their rest position parallel to the applied electric field direction while the anions are displaced in the opposite direction, resulting a net dipole moment in the direction of the field (Viswanathan, 2006). In the presence of electric field, these ions will be displaced and slightly shifted from their rest positions. The cations are displaced in the direction of electric field while anions are displaced in the opposite direction (Wert and Thomson, 1970; Viswanathan, 2006; Naumann, 2008).

In materials which consist of permanent dipoles, the dipolar polarizabilty occurs as the permanent dipoles tend to change their orientation and align along the direction of the applied electric field (Wert and Thomson, 1970; Karasz, 1972; Ku and Liepins, 1987).

Another contribution to polarization is space charge (Sirdeshmukh et al., 2006), or the accumulation of mobile charges at structural surfaces and interfaces. Rather than being a direct property of a material this is only a feature of heterostructures (Ishida, 1994). Fig. 2.2 illustrates the polarization effect in a dielectric at a range of frequency.

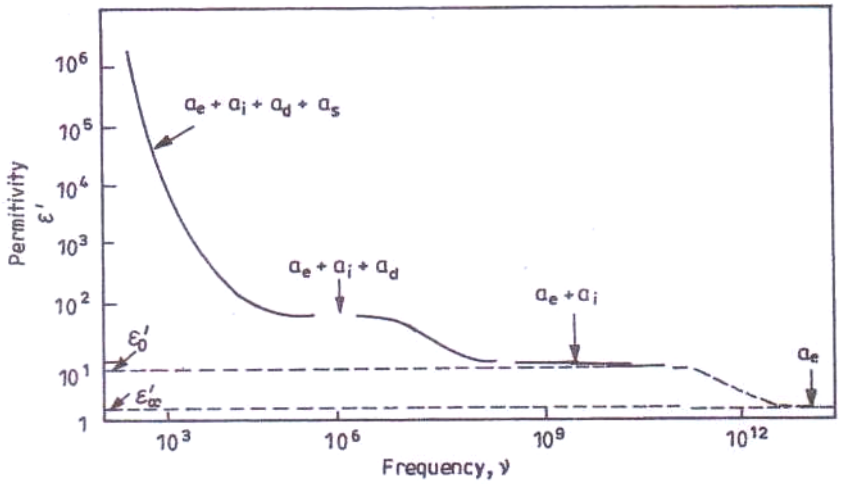

Fig. 2.2. Polarization effect in a dielectric (Viswanathan, 2006).

2.4 Dielectric loss

The loss of energy in dielectric dissipated in the form of heat which generated when the dipole is oscillated in the presence of an alternating field (Naumann, 2008). There are two main forms of loss within dielectric. First is due to conduction and the other is due to relaxation effects (Sirdeshmukh et al., 2006). In conduction loss, a flow of charge through the material causes energy dissipation. Dielectric loss is the dissipation of energy through the movement of charges in alternating electromagnetic field as polarization switches direction. Conduction loss shows a linear log (tan δ) versus frequency plot, while the loss due to relaxation effects shows a maximum at a certain frequency. The total contribution to dielectric loss is the sum of conduction and relaxation effect. The net effect on the appearance of the curve

when both effects are present will be a peak superimposed on a straight line (Sirdeshmukh et al., 2006).

Dielectric relaxation can be described generally as the lag in the response of a system to change parallel with the forces to which it is subjected. In the presence of electric field, polar molecules of a system rotate toward an equilibrium distribution in molecular orientation with a corresponding dielectric polarization (Wert and Thomson, 1970). The polarization forming can be rapid or slow, dependent on the type of polarization such as electronic polarization in which the polarization process usually requires shorter time than atomic and ionic polarization. In a heterogeneous of material, there is interfacial polarization, arises from the accumulation charges at the interfaces of two phases which differ in dielectric constant and conductivity. If the difference of conductivity between the two phases is high, therefore the polarization might occur rapidly and can be observed in the radio-frequency range, meanwhile if the difference is low, it might take seconds or minutes to be observed at a low frequency (Symth, 1955).

The presence of frictional resistance in a dielectric medium influences the time required to polarize and additionally high internal frictional resistance may make it difficult for the dipole to change state and hence lengthen the time required for the polarization. As the dipole is oscillated in the presence of an alternating field, energy is being dissipated in the form of heat into the material presented as dielectric loss (Smyth, 1955; Naumann, 2008).

The presence of some impurities would increase the conductivity of a dielectric material; this type of impurities can also result in large increase in the dielectric loss (Barsoum, 2003). The lower the dielectric loss the more effective the dielectric acts as an insulator. In most of the cases, it is desirable to have dielectric loss as minimum as possible, nevertheless in certain cases, dielectric loss is essential in application which requires heat especially in microwave oven.

2.5 Dielectric Applications

A major used of dielectric is in fabricating capacitor. Basically, a capacitor is a dielectric material sandwiched between conductive plates. Besides capacitor, dielectrics are also employed as insulation for wires, cables, and electrical equipment, in apparatus used for the propagation or reflection of electromagnetic waves, and for a variety of artifacts, such as rectifiers and semiconductor devices, piezoelectric transducers, dielectric amplifiers, and memory elements (Jiang et al., 2006; Yim et al., 2006; Subodh et al., 2007; Thomas et al., 2008).

Capacitor is defined as two parallel conductive plates which are close to each other connected in an electrical circuit (Pollock, 1993; Viswanathan, 2006). The function of a capacitor is to store an electrical charge when subjected to an electric field. Each capacitor has a capacitance C, the measure of the ability of the two plates to store charges, which have the standard units of Farads (F). The capacitance is defined by the relationship Q = CV where Q is the charge on each capacitor plate and V is the voltage between capacitor plates. The capacitance, C involves both geometrical and a material factors which represents by equation 2.5 (Viswanathan, 2006). Most capacitors consist of ceramic or plastic dielectrics or the combination of

both which better known as organic-inorganic composites. Ceramic capacitor is usually bigger in size and has geometry of rectangular shape. The difficulty in processability to form thinner and variety shapes of dielectric is restricted by their brittle nature behaviour. Ceramic capacitors are widely utilized in high power application due to their high dielectric constant (Xie et al., 2004; Sonoda et al., 2011).

On the other hand, plastic capacitors are mostly seen in thinner size. They have a high flexibility which makes them possible to be shaped into variety shapes such as thin film which satisfies the demand on much lighter and smaller devices. Plastic capacitor has much lower dielectric constant which seen them are widely utilized low-k application like fast signal propagation (Jiang et al., 2006).

2.6 Polyimide

Polyimides are primarily applied in aeronautical and space, automotive, office automation, electrical, industry and vacuum technology. They have been used as self-lubricant, bearings, insulators, packaging, dielectrics, sealers, membrane, photoconductor, light emitting, and as a joint part (Kuntman and Kuntman, 2000; Seckin et al., 2010) owing to their excellent thermal stability, chemical and solvent resistance, good mechanical and electrical insulating properties (Song et al. 2002; Chung and Hsiao., 2008; Chen et al., 2009). The linearity and stiffness of the aromatic backbone of the polyimide imparts good thermal stability while at the same time long, linear ordered chains makes polyimide a good solvent resistance (Hedrick et al., 1997; Dunson, 2000).

Nowadays, polyimides are commercially used in microelectronic industries as packaging materials, circuit boards, interlayer dielectrics, coating and for passivative protection especially in high temperature and high stress application (Simpson and St.Clair, 1997; Chang et al., 2009; Sebastian et al., 2009). Possessing low dielectric constant ascribes to its high free volume makes polyimides become one of the dominant materials used as dielectrics in intergrated-circuit designs where some issues are concerned such as the resistance-capacitance (RC) time delay, cross-talks, and power dissipation. These issues can be minimized by using low dielectric materials with good thermal stability, excellent radiation and high mechanical strength (Deligoz et al., 2005; Lin and Wang et al., 2007; Chang et al., 2009). Apparently, polyimides meet most all these requirements. As technology is rapidly growing, polyimides have been altered to meet the demands by customers and also to keep up with the advancements.

Polyimide is a specialty polymer based on stiff aromatic backbones (Volksen, 1994; Dunson, 2000). Commercially, there are three basic types of polyimides which classified as condensation cured, addition cured and photocured available (Licari, 2003). These types are differing in their molecular structure, curing process and properties. However, condensation cured polyimides is commonly used and practiced since decades ago (Volksen, 1994; Chilton, 1995; Biron, 2004). Condensation-cured polyimides start as polyamic-acid precursors dissolved in an organic solvent which is obtained from solution polycondensation of an aromatic diamine and dianhydride or polyamic ester (Dunson, 2000; He and Ping, 2003; Licari, 2003). This type of polymer is widely used in fabricating electronic devices.

Polyimides have various structures which prepared by variety of monomers by several synthetic routes (Chiang et al., 2004). The structure of the polyimides can be altered and it has tremendous effects on the properties of the polyimides (Ding, 2007). The flexibility of their chains is much dependent on the types of monomer used (Cho et al., 1997; Hsiao et al., 1998; Hergenrother et al., 2004**).** Liaw et al., (2001) reported that the new five benzene rings-containing diamine, α,α′-bis[3,5-dimethyl-4-(4-aminophenoxy)phenyl]-1,4-diisopropylbenzene **(**BDAPD**)** containing flexible ether and isopropylidene units, and five benzene rings was synthesized and used to prepare a series of transparent, flexible and tough polyimide films. The presence of flexible ether in the diamine helped in increasing the solubility and moldability of the polyimide. Hundreds of polyimides with different chemical structure and molecular order and accordingly, different physical, mechanical and chemical properties have been reported (Liou et al., 1999; Song et al., 2002).

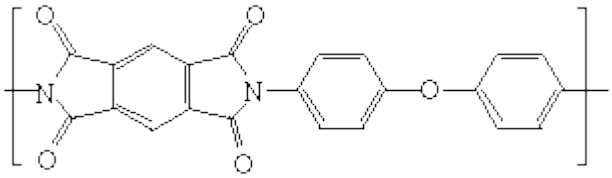

Fig. 2.3. Polyimide structure based on PMDA and ODA monomers (Takekoshi, 1996).

2.6.1 Two-step synthesis method

Two-step synthesis is a classical method which involves the polymerization of a soluble poly(amic acids) intermediate before thermally cured at certain temperatures to yield a final polyimide (Sroog et al., 1965; Volksen, 1994). The initial step of this synthesis route is the preparation of poly(amic acids) solution by dissolving the aromatic diamine in a polar solvent before adding a dianyhydride into it. Meanwhile, the second step involves the imidization or cyclodehydration reaction

of poly(amic acids) by heating the film to the elevated temperature (Dunson, 2000). This process was introduced by Dupont in 1950's which is the most practised and referred by manufacturers and researchers until today (Sroog et al., 1965).

In polyimide synthesis, many factors affect the process and hence the polyimide properties. The molecular weight of the polyimide is not only dependent on the monomers used but also both of reaction conditions and mode of monomer addition must be taken into account (Bower and Frost, 1963; Volksen, 1994). The molecular weight of polyimide prepared at lower reaction temperature is reported to be higher than those prepared at higher temperature (Dunson, 2000). Meanwhile, the order of monomer addition greatly influences the final molecular weight of the polyimide as it is found that the polyimide with higher molecular weight is obtained when solid dianhydrides are added into diamines solution but not vice versa (Bower and Frost, 1963; Dine-Hart and Wright, 1967). The monomers are usually varied to obtain the desirable properties (Song et al., 2002). Kapton^{TM} is the first commercial polyimide to enter the market (Sroog et al., 1965). The reaction scheme of two-step method is illustrated in Fig. 2.4 in which pyromellitic dianhyride (PMDA) and 4,4'-oxydianiline (ODA) monomers are taken as example.

2.6.2 Formation of poly (amic acids)

The formation of the intermediate poly(amic acids) is derived from diamine and dianhydride in a dipolar aprotic solvent through the nucleophilic attack of the amino group on one of the carbonyl carbons of the anhydride group (Dunson, 2000). The nitrogen from the aromatic diamine attacks the unshared pairs of electrons of

anhydride group. Poly (amic acids) formation is an exothermic reaction and the molecular weight of the product is dependent on the reaction rate.

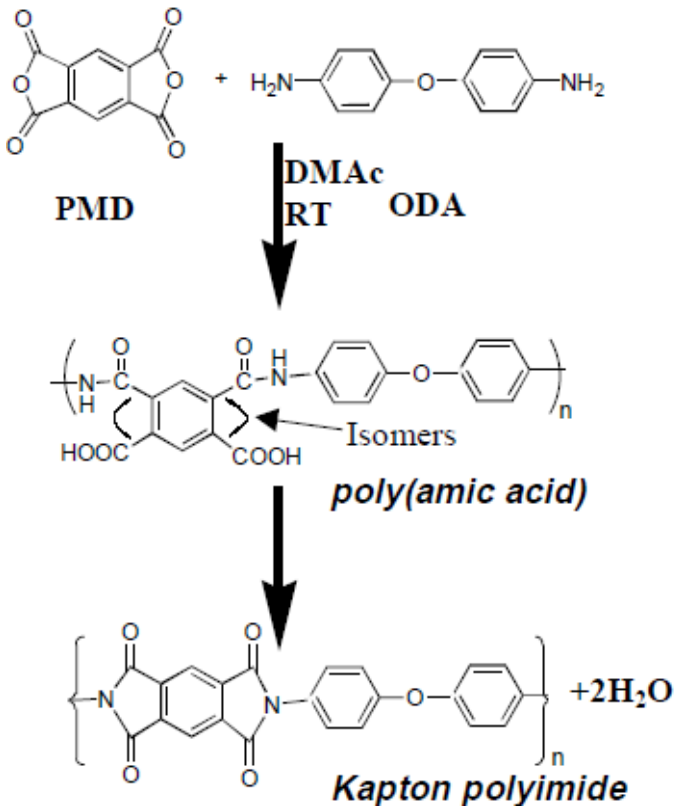

Fig. 2.4. Reaction scheme for the preparation of kapton polyimide (Takekoshi, 1996).

2.6.3 Thermal imidization

The poly(amic acids) solution is usually casted into a suitable substrate such as a clean and dry glass dish before gradually heated or imidized at certain temperatures to eliminate the solvent and undergoes a thermal curing which usually ranging from 50-400^{o}C (Sroog, 1976; Takeichi et al., 1999; Saeed et al., 2006). Many have suggested different thermal routes of PAA to ensure 100% imidization. Some require the PAA to be dried at lower temperature for a longer time for example

at 70^{o}C for 24 hours, before stepwisely heated at different temperatures; 100^{o}C, 250^{o}C, 350^{o}C for one hour respectively (Xie et al., 2005; Li et al., 2007; Xiao et al., 2010) to minimize shrinkage. However, need to be taken into consideration is the presence of water in PAA which would cause degradation, voids and film shrinkage (Dunson, 2000). Another often practised thermal route is the PAA is gradually heated at 100^{o}C and hold for 1 hour, from 100^{o}C to 200^{o}C for one hour, 200^{o}C to 300^{o}C and slowly cooled to RT (Brandom and Wilkes, 1994; Deligöz et al, 2005; Deligöz et al., 2006).

Nevertheless, both ways are proved to be effective and right as the PAA solution is completely imidized to PI. The degree of imidization is defined by the area ratio and the appearance and disappearance of significant bands in PI and PAA spectra studied through FTIR result.

2.7 Inorganic materials

2.7.1 Aluminium Oxide

Aluminium oxide or alumina is an amphoteric oxide of aluminium with the chemical formula of Al_2O_3. Alumina has a corundum structure (Callister, 2003). The oxygen ions are hexagonally close-packed and the Al ions fill two-thirds of the available octahedral sites (Barsoum, 2003).

Alumina is a dominant ceramic used in wide applications due to its high thermal stability and good thermal conduction, superior mechanical properties as it possesses high resistance to abrasion and high hardness. (Goswami et al., 2002; Wu et al., 2005). The thermal conductivity of Al_2O_3 is around 30-35 W/(m.K) (Barsoum,

2003). It also exhibits low electrical losses, low electrical conduction and also possesses high dielectric strength (Malec et al., 2010). The dielectric constant of Al_2O_3 is reported to be in a range of 8-10 (Li et al., 2007). Its excellent insulator properties make it adaptable for use in numerous applications includes as electronic substrates, spark plug insulators and even as magnetohydrodynamics (MHD) power generators (Goswami et al., 2002).

2.7.2 Barium Titanate

Barium titanate has perovskite crystal structure which have two cations consists of Ba^{2+} and Ti^{4+}. Barium titanate goes through phase transitions upon heating from rhombohedral to cubic as following (Barsoum, 2003):

$$\text{Rhombohedral} \xrightarrow[-90^{o}C]{} \text{orthorhombic} \xrightarrow[0^{o}C]{} \text{tetragonal} \xrightarrow[130^{o}C]{} \text{cubic}$$

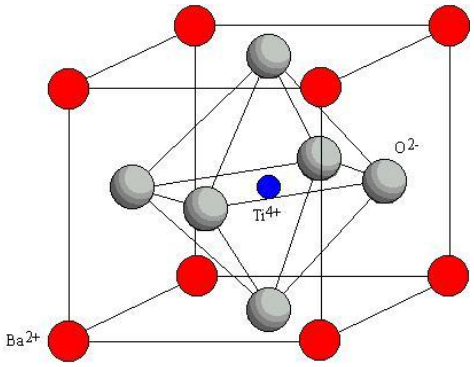

Fig. 2.5. A unit cell for the perovskite structure of $BaTiO_3$ (Viswanathan, 2006).

At temperatures above 130^{o}C, the crystal structure is cubic. Ti^{4+} ion is centered in the unit cell with Ba^{2+} ions are situated at all eight corners of the cube while O^{2-} ions located at the center of each of the faces (Barsoum, 2003; Callister, 2003). However, between 130 and 0^{o}C, $BaTiO_3$ has a distorted perovskite structure

with an eccentricity of the Ti^{4+} ions and displacement of O^{2-} from its symmetrical position and Ba^{2}+ ions at the corners of the unit cell which is of tetragonal symmetry in which a cube that has been elongated slightly in one direction. This positioning of the Ba^{2+}, Ti^{4+} and O^{2-} ions within the unit cell resulting in spontaneous polarization which is the polarization in the absence of an electric field. This behaviour has made $BaTiO_3$ being classified as ferroelectric material. This ferroelectric characteristic of $BaTiO_3$ has made it as a dominant dielectric material in capacitor owing to its high dielectric constant which is around 2000-5000 at room temperature (Viswanathan, 2006), low dielectric loss, and high dielectric breakdown strength (Eckert et al., 1996; Zhou et al., 1997; Maison et al., 2003; Wang et al., 2009).

$BaTiO_3$ has been utilized in many applications especially in electric industry which have seen them being used as pyroelectric detectors, ferroelectric memories, sensors, positive temperature coefficient (PTC) thermistors (Phule et al., 1990; Sharma and Sarma, 1998; Gablenz et al., 2001) and moreover $BaTiO_3$-based dielectrics have been dominated the multilayer ceramic capacitors (MLCCs) since 1950s (Kusters et al., 1994).

2.7.3 Titanium Oxide

Titanium oxide or titania (TiO_2) exists in three modifications with different crystal lattice structures and therefore altering properties. Rutile, anatase and brookite are three different structure of titania (Mardare et al., 2009). Rutile form is the most stable form. Meanwhile, anatase and brookite rearrange at elevated temperature of 750^{o}C or 950^{o}C monotropically to rutile. Anatase has a cubic close packing of the oxygen atoms, in which half of the tetrahedral spaces are filled with

titanium atoms. Meanwhile, rutile has a hexagonal close packing of the oxygen atoms, in which half of the octahedral spaces are filled with titanium atoms (Winkler, 2003).

Titania has drawn great interest due to its high catalytic, photostability, good chemical stability, nontoxicity in addition of low cost (Tsai et al., 2006; Mardare et al., 2009; Chen et al., 2008). Titania has versatile functions due to its different phases which has its own properties and made them being utilized in various applications. Having a remarkable activity and non-toxic properties, anatase TiO_2 becomes one of the best photocatalyst and it is also being used in photochemical solar cells and gas sensors (Zhang et al., 2007; Kim et al., 2007; Epifani et al., 2008). As in capacitor fabrication and microelectronic devices, rutile TiO_2 is being utilized attributed to its high resistivity and high dielectric constant. The dielectric constant of TiO_2 is reported to be in range of 14-114 (Viswanathan, 2006). Apart from that, rutile is also becomes one of the important biocompatible materials (Mardare et al., 2009).

2.7.4 Zirconium Oxide

Zirconium oxide is inorganic metal oxide that is mainly used in ceramic materials. Zirconia goes through three phases upon heating less than 1atm pressure. It transforms from monoclinic to cubic before reaching its melting point. The low-temperature phase is monoclinic, stable to 1170^{o}C at which temperature it changes reversibly to the tetragonal phase, which in turn is stable to 2370^{o}C. Above that temperature the cubic phase becomes stable up to the melting point of 2680^{o}C (Barsoum, 2003). The transformation of the phases is summarized as following:

$$\text{Monoclinic} \xrightarrow[1170^{o}C]{} \text{tetragonal} \xrightarrow[2370^{o}C]{} \text{cubic} \xrightarrow[2680^{o}C]{} \text{liquid}$$

Zirconia has superior thermal stability properties as it does not melt below 2680^{o}C make it well known as one of the excellent refractory materials. It is non-magnetic and highly resistant against acids, alkaline lyes, and exogenous (chemical, thermal and mechanical) influences. In addition, it has a high mechanical stability and is very resistant to abrasion. Zirconia-based materials among the most important oxygen ion conducting solid electrolytes, owing to their applications in technologically important devices which include solid oxide fuel cells, oxygen sensor, oxygen pumps and thermal barrier coatings (Izumi et al., 1989; Riegel et al., 2002; Huang et al., 2008). The dielectric constant of ZrO_2 also is quite high which is around 12-28 (Harrop and Wanklyn, 1967).

2.8 Organic/Inorganic composite

Organic/inorganic composite has been extensively studied over the past two decades and has drawn a tremendous attention due to their unique properties which integrates the advantages of both organic and inorganic materials and hence performs far beyond those of the individual constituents (Yen et al., 2003; Murugaraj et al., 2005; Jacob et al., 2009). Organic-inorganic composites have been applied in various fields and in fact have been dominating the microelectronics industry for past few decades (Schmidt, 1996; Zhang et al., 1997; Gómez-Romero et al., 2003; Sanches et al., 2005). They are mostly used as coating materials, dielectrics and packaging materials in electrical industries while the demand for organic/inorganic composites from various fields are growing which find application in various fields such as membranes in fuel cell application (Gaowen and Zhentao, 2005; Nagarale et al., 2010).